Early Journal Content on JSTOR, Free to Anyone in the World

This article is one of nearly 500,000 scholarly works digitized and made freely available to everyone in the world by JSTOR.

Known as the Early Journal Content, this set of works include research articles, news, letters, and other writings published in more than 200 of the oldest leading academic journals. The works date from the mid-seventeenth to the early twentieth centuries.

We encourage people to read and share the Early Journal Content openly and to tell others that this resource exists. People may post this content online or redistribute in any way for non-commercial purposes.

Read more about Early Journal Content at http://about.jstor.org/participate-jstor/individuals/early-journal-content.

JSTOR is a digital library of academic journals, books, and primary source objects. JSTOR helps people discover, use, and build upon a wide range of content through a powerful research and teaching platform, and preserves this content for future generations. JSTOR is part of ITHAKA, a not-for-profit organization that also includes Ithaka S+R and Portico. For more information about JSTOR, please contact support@jstor.org.

XV.

On Two New Crystalline Compounds of Zinc and Antimony, and on the Cause of the Variation of Composition observed in their Crystals.

BY JOSIAH P. COOKE, JR., A.M.,

ERVING PROFESSOR OF CHEMISTRY IN HARVARD UNIVERSITY.

(*Communicated June* 27, 1854.)

THE metallic alloys have not received that share of investigation which their importance would seem to demand; nevertheless, the researches which have been made during the last twenty years are sufficient to refute the formerly received opinion, that they are all merely mechanical mixtures. In 1830, F. Rudberg,* while determining the latent heat of the alloys of tin and lead, observed that, when the proportions of the two metals corresponded to $PbSn_3$, the temperature of the melted alloy fell uniformly to the point of fusion, 187° C., where it remained constant for some minutes, owing to the escape of latent heat. If, however, the metals were mixed in other proportions while the same fixed point was observed, he found that the thermometer also stood still at a second and higher point, which approached nearer and nearer the point of solidification of lead or tin, according as the alloy contained a greater excess of one or the other of these two metals. From these facts he concluded that the alloy $PbSn_3$ was a definite chemical compound, having but one point of solidification, and that the other alloys were mixtures of this compound with one or the other metal, and that the two stationary points of temperature corresponded, the lower to the point of solidification of $PbSn_3$, the higher to that of tin or lead, according as one or the other was present in excess. Similar phenomena were afterwards observed in several other alloys, especially in the ternary alloys of zinc, tin, and lead, which were shown by the Messrs. Svanberg,* on the same grounds, to contain a definite compound, $ZnSn_3, 2\,PbSn_3$. The fact that, in a melted mixture of bismuth and zinc, which do not alloy together, there are two stationary points of temperature coinciding very closely with the melting points of the two metals, seems to support Rudberg's opinion.† It is well known that Newton's (or Arcet's) alloy $Bi_3Pb_2Sn_2$, after it has been rapidly cooled from a melted condition to 57° C., or even a few degrees lower, becomes suddenly heated by a spontaneous evolution of heat, accompanied with a very considerable expansion of the mass. Since, after the expansion, the specific heat of the alloy is the mean of that of the metals which compose it, and since the change is accompanied with a manifest alteration of texture, Person ‡ argues that the phenomenon indicates an actual chemical decomposition in the whole mass of the alloy, and that the combination between the metals is only momentary, and confined within certain temperatures. Similar facts he shows to be true of Rose's alloy Bi_2PbSn_2, and also of Bi_3Pb_2 and Bi_3Sn_4.

---

* Poggendorf, *Annalen*, Vol. XVIII. p. 240.

Croockewit,§ by melting together copper, tin, lead, and zinc in different atomic proportions, stirring the melted metals while cooling, and after partial solidification turning out the still fluid portion, obtained crystalline masses which, as he found by analysis, approached, and sometimes very closely coincided with, the calculated composition of Cu_2Sn_5, $CuSn$, Cu_2Sn, Cu_3Zn_5, Cu_3Zn_2, Cu_2Zn, Cu_2Pb_3, $CuPb$, $SnZn_2$, $SnZn$, Sn_2Zn, $SnPb_2$, $SnPb$, Sn_3Pb_2. He obtained, moreover, similar results in regard to the amalgams, though not quite so satisfactory, and draws the conclusion, that the binary alloys of these metals are mixtures of the above compounds either with each other or with one or the other of the metals. Rieffel || makes seven different compounds of tin and copper, $CuSn$, $CuSn_{24}$, $CuSn_{48}$, $SnCu_{24}$, $SnCu_{48}$, $SnCu_{72}$, $SnCu_{96}$, of which $CuSn$ "crystallizes in large and exceedingly characteristic plates," and $CuSn_{24}$ and $CuSn_{48}$ "both in needles radiating in all directions from numerous centres." These compounds do not correspond to those of Croockewit, and the discrepancy is probably owing to a variation in composition similar to that, hereafter to be explained, in the compounds of zinc and antimony, which will be found to resemble those of copper and tin, as described by Rieffel, at least in their crystalline characters.

---

[*] Poggendorf, *Annalen*, Vol. XXVI. p. 280.

[†] M. Fournet, *Ann. de Chim. et de Phys.*, Vol. LIV. p. 247.

[‡] Ibid., Vol. XXIV. pp. 143, 148.

[§] *Journal für prakt. Chemie*, Vol. XLV. p. 87.

[||] *Compt. Rend.*, Sept., 1853, p. 450.

Quite recently Levol* has examined the alloys of copper and silver, of copper and gold, and of lead and silver, in regard to their chemical constitution, starting on the supposition that these metals are capable of forming definite chemical compounds with each other, and that the ordinary alloys employed in coinage and in the arts are mixtures of such compounds and an excess of metal, and moreover considering as proved, that, when such melted alloys cool slowly, these compounds tend to separate from the metal, producing inequality of composition in the cast lingot, so that homogeneity in such cases is an indication of definite composition. In the alloys of copper and silver, Ag_3Cu_4 was the only one of which the lingots carefully cast in spherical or cubical moulds were found, by analysis of portions taken from the interior and exterior of the mass, to have a uniform composition throughout. The alloys either of copper or silver with gold were all found to give homogeneous lingots, and the reverse was the case with the alloys of lead and silver, except $PbAg_{100}$. If the hypotheses from which this investigation starts are assumed to be correct, the conclusions to be drawn from the results are, — 1st, that the only definite compound of copper and silver is Ag_3Cu_4; 2d, that either gold is not capable of forming a definite compound with silver or with copper, or else that their compounds, being isomorphous with each other and with the metals, are capable of mixing uniformly in any proportions; 3d, that lead and silver do not form with each other any definite compounds.

Karsten† found that dilute sulphuric acid or a solution of sulphate of copper is not decomposed by alloys of zinc and copper when the zinc equals or exceeds the proportion corresponding to ZnCu; also that nitric acid or a solution of nitrate of silver is not decomposed by alloys of copper and silver when the amount of silver exceeds or equals that of CuAg. If, however, the zinc in the first, and the copper in the last, were in excess, he observed that decomposition took place, and continued until these metals were completely removed from their respective alloys, and pure copper or silver left. He opposes the opinion that these alloys are mixtures of a definite compound with an excess of one or the other metal, arguing that, if this were the case, the acids would dissolve only the excess of metal, and leave the compounds ZuCu and CuAg.

The above are the most important investigations, bearing directly on the chemical nature of metallic alloys, which have fallen under the notice of the author, and they concur to support the opinion that, in many cases at least, the metals tend to unite in definite proportions. The alloys of zinc and antimony, which form the subject of this memoir, do not appear to have been included in any of these investigations. The previous knowledge in regard to them is given by Gmelin in his text-book in the following words: "These two metals fuse together with facility, and, according to Gehlen and A. Vogel, without emission of light, and form a hard, brittle, steel-colored alloy, whose density is less than the medium density of its elements (Gellert)." *

---

* *Annales de Chimie et de Physique*, Vol. XXXVI. p. 193, and Vol. XXXIX. p. 163.

† Poggendorf, *Annalen*, Vol. XLVI. p. 160.

It will be the object of the present memoir to show, first, that zinc and antimony form with each other two, and probably only two, definite compounds; secondly, that these compounds are capable of a very large variation in composition without any change in the crystalline form; and lastly, that this variation can only be explained by admitting an actual perturbation in the law of definite proportions produced by the influence of mass. The two compounds are

I. *Terantimonide of Zinc, or Stibiotrizincyle,* $SbZn_3$.

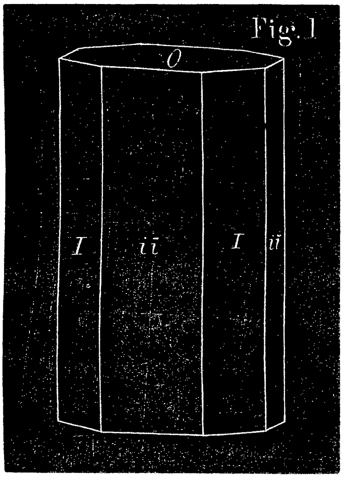
This may be best prepared by melting together 57 per cent of antimony and 43 per cent of zinc,† and allowing the liquid mass when thoroughly mixed to cool until a crust forms on the surface. On piercing through this crust, and turning out the still liquid alloy, the crucible, if broken open when cold, will be found filled with the most beautiful prismatic crystals. These crystals are obtained in their greatest perfection by employing eight or ten pounds of the alloy, and cooling the crucible very slowly in sand. In order to insure a constant composition of the alloy, it is best to melt the antimony first, and afterwards add the zinc in small portions, removing the crucible from the fire as soon as the whole is melted, and stirring with a heated earthenware rod. Moreover, in order to prevent oxidation of the crystals, it is important that the hole pierced through the crust should be quite small, and it requires a little practice to catch the exact moment when the crust is thick enough to support the mass of melted metal in the crucible.

The crystals thus obtained present the following properties. They have a very brilliant metallic lustre and a silver-white color; (the surfaces are often, however, iridescent, owing to a slight oxidation, and the true color is then only seen on the fracture.) They are very brittle, and can readily be reduced to a grayish-white powder. Their hardness = 3.5. The Sp. Gr. varies with the composition, as will be shown hereafter; that of crystals containing 43 per cent of zinc = 6.327 nearly. The form is a rhombic prism belonging to the Trimetric System, with sometimes only one, but generally with both sets of lateral edges truncated. The crystals almost invariably, so far as I have observed, run out to fine points, and although I have examined many hundreds, I have only met with a very few having the basal plane *O*, and with none on which planes modifying the basal edges could be distinguished. It was, therefore, only possible to ascertain the relative size of the lateral axes. This is given below under Fig. 2. Fig. 1 exhibits the general form of the isolated crystals supplying the terminal plane *O*.

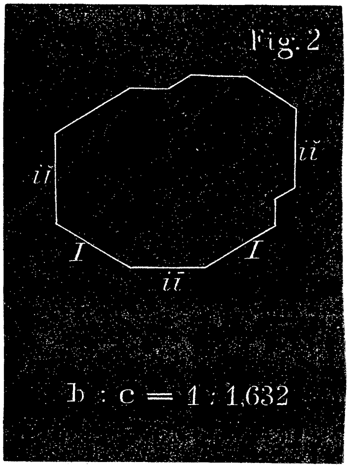
---

* Gmelin's *Hand-Book*, Cavendish ed., Vol. V. p. 50.

† When the metals are not pure, it is best to make allowance for the impurity.



I on i ī = 148° 30′.
I on i ĭ = 121° 30′.
I on I = 117° or 63°.



I in 1 on I in 2 = 117°.
i ĭ in 2 on I in 1 = 121° 30′.
i ĭ in 1 on I in 1 = 121° 30′.

The faces of the crystals are generally striated, but from a quantity of them several can almost always be obtained whose faces reflect a very well defined image, so that the angles can be measured with the greatest accuracy. The angles as above given measured the same on a large number of crystals from several different crystallizations, and in cases where a variation from them was observed it was evidently the result of striation or of some imperfection. The measurements were made in a darkened room, using as a signal a narrow horizontal slit in the screen which covered the window illuminated by the sun. This simple arrangement, for which I am indebted to Professor Miller of Cambridge, England, enabled me to determine the angles even of the smallest crystals with great precision. The isolated crystals of $SbZn_3$ obtained as described above are small, a few tenths of a line only in diameter, and not generally over an inch in length. They tend, however, to form compound crystals with parallel axes, which are often several inches in length, and a quarter of an inch or more in diameter. Fig. 2 is a section of a very well formed double crystal, on which all the angles were accurately measured. A few of these angles given beneath the figure show that the character of the combination is as described. The crystals do not have any distinct cleavage, but it is possible that the basal plane O, which, as before stated, is seldom seen, may be a cleavage plane.

The composition of the crystals of $SbZn_3$ varies, as will hereafter be shown, with the composition of the alloy in which they form. The crystals whose analyses are given below were prepared by melting together 58 per cent of commercial antimony and 42 per cent of zinc. The zinc was melted first, and when in fusion the antimony was added. This involved a greater loss of antimony than if the opposite course had been followed, as recommended above, which, with the impurity of the metal,* had the effect of increasing the percentage of the zinc in the alloy about eight tenths of one per cent. The crystals may therefore be regarded as having formed in an alloy whose composition approximated closely to Sb. 57.2 per cent, Zn 42.8 per cent. The analyses 1, 2, and 3 were made by myself, of crystals from as many different crystallizations. The fourth column gives the calculated composition of $SbZn_3$ on the supposition that the equivalent of antimony = 129.032, and that of zinc = 32.527, as is generally received.

	1.	2.	3.	4.
Antimony, . .	57.24	56.50	56.93	56.93
Zinc, . . .	42.83	43.06	43.15	43.07
	100.07	99.56	100.08	100.00

From these analyses it appears that an alloy which contains 42.8 per cent of zinc yields crystals of the same composition with itself, and corresponding to the calculated composition of $SbZn_3$.

The most characteristic property of the new compound is its strong affinity for oxygen, which gives it the power of decomposing water with rapidity at the boiling point. This property led in fact to its discovery. The author, while washing with hot water some granulated alloy, having the composition of $SbZn_3$, which had been used for preparing antimoniuretted hydrogen, observed that the metal continued to evolve gas after the last trace of acid had been removed. The singular phenomenon was at first referred to an increased activity of the zinc in the alloy, produced by the galvanic action of the particles of antimony set free by the action of the acid. This theory was soon, however, disproved, by the fact that an alloy of the same composition, which had not been acted on by acids, when placed in boiling water, produced the same action, though in a less degree, and by the no less important fact, that the rapid evolution of gas could only be produced with alloys containing about 43 per cent of zinc.* Two hundred grammes of this alloy granulated to about the size of fine shot evolved one hundred and thirty centimetres of cubes of gas in ten minutes. When previously treated with a few drops of a solution of bichloride of platinum, and afterwards washed, the amount of gas was nearly doubled. The same quantity of alloy which had been previously treated with hydrochloric acid, and then thoroughly washed, gave, when boiled with water, nearly a litre of gas in the same time. The gas evolved was pure hydrogen, as is shown by the following experiments.

---

* The zinc used in these experiments was nearly pure. The antimony was a good article of commercial antimony, containing about one per cent of impurity, which, with the exception of a slight trace of arsenic, was not taken up by the crystals.

1st. The gas evolved from an alloy containing 50 per cent of zinc, which had been previously treated with hydrochloric acid, and then washed, was burnt in Regnault's eudiometer, with the following results: —

Tension of gas, ...	0.379	metres.
" " gas + oxygen, ...	1.219	"
" " oxygen after combustion, ...	0.653	"
" " gas consumed, ...	0.565	"

$0.566 \times \frac{2}{3} = 0.378$, tension of hydrogen consumed.

2d. Gas evolved from water and alloy at 100° C., but not in ebullition, was passed through hot concentrated nitric acid for six hours, about two bubbles passing a second. The acid, afterwards evaporated to dryness, and the residue dissolved in hydrochloric acid, diluted and treated with sulphuretted hydrogen, gave no indication of antimony.

3d. The gas evolved during violent ebullition gave, under the same treatment, a trace of antimony, which was evidently carried over by the stream in mechanical suspension. Both experiments were repeated twice, with the same results.

4th. The gas from an alloy of commercial metals, passed for several hours through a small tube of Bohemian glass heated to redness, gave a slight mirror of arsenic.

5th. The gas from an alloy of pure metals gave no metallic mirror under precisely the same circumstances as in the last experiment.

From all these results, indicating, as they do, an analogy between $SbZn_3$ and the well-known metallic radicals of Organic Chemistry, it was naturally inferred that it would be easy to prepare from it a large number of compounds; but although the first qualitative experiments seemed to verify this assumption, it afterwards proved to be unfounded. The first action of chemical agents on $SbZn_3$ is similar to their action on the simple metals, but before the reaction is terminated and a definite compound formed, the radical is decomposed, and compounds of the separate elements alone result. Thus, when the powdered $SbZn_3$ is boiled with water, the first effect, as is sufficiently evident from the above experiments, is a direct oxidation of the alloy; before, however, the whole is oxidized, a grayish-white powder is formed, from which hydrochloric acid dissolves a large amount of oxide of zinc, and a very small amount of oxide of antimony.* The instability of this singular substance will also appear from the following experiments.

---

* See Table on subsequent page of this memoir.

1st. Exposed to the action of chlorine gas, powdered $SbZn_3$ inflamed, and a mixture of the chlorides of zinc and antimony was formed.

2d. A solution of iodine in strong but not absolute alcohol converted the same powder into a yellow substance, which proved to be an oxyiodide of antimony, and into iodide of zinc, which was found in solution.

3d. Bromine dissolved in alcohol formed, with the powder, bromide of zinc, which dissolved, and oxide of zinc, which is insoluble. The small amount of water which the strong alcohol contained was, as is evident, essential to these reactions, and on using solutions of iodine and bromine in absolute alcohol, little or no change could be observed.

4th. Dry oxygen was passed over a weighed portion of finely powdered $SbZn_3$ contained in a glass bulb, which was gently heated with a spirit lamp. When the temperature was yet much below ignition, the mass suddenly glowed throughout like tinder, and changed into a white powder, which the increased weight proved to be a mixture of ZnO, SbO_5, and SbO_4.

Weight of powdered $SbZn_3$, ...	0.4647
“ “ oxygen absorbed, ...	0.1235
“ “ oxygen required to form $3\ ZnO + \frac{1}{2}\ SbO_4 + \frac{1}{2}\ SbO_5$,	0.1231

---

* Dr. A. A. Hayes, of Boston, has had the kindness to submit some crystals of $SbZn_3$ to his new process of analysis by electrolysis, thinking that under the influence of a feeble galvanic current they might act as a radical. He found that at first they seemed to act in this way, both the zinc and antimony entering into solution; but that, before the process was finished, decomposition ensued, after which the zinc only dissolved.

On attempting to moderate the action by using a lower temperature regulated by a bath of fusible metal, little or no change resulted.

5th. A few grammes of very finely pulverized crystals of $SbZn_3$ were covered in a thick glass flask, with about twice their bulk of iodide of ethyle, and the hermetically sealed vessel exposed to a temperature of about 150° C. in a Papins digester, for several hours. On opening the flask when cold, it was found to contain a white crystalline solid, which was readily purified by dissolving in alcohol and recrystallizing. There separated from the alcoholic solution needle-shaped crystals, which were also soluble in water. They were found to melt at about 140° C. to a yellowish fluid, and when heated in the air to about 190° C., boiled, forming a dense white smoke, which condensed on the sides of the tube to a white amorphous powder. The smoke had a strong and disagreeable alliaceous odor, probably due to stibethyle. The crystals have also a slight alliaceous odor, and a bitter metallic taste. Their solution in water gives with test-paper the reaction of the feeble acids. An analysis conducted in the usual way gave the following results : —

	Found.	Calculated.
Hydrogen, . . .	3.53	3.47 = H_{25}
Carbon, . . .	16.91	16.67 = C_{20}
Zinc, ...	9.03	9.03 = Zn_2
Antimony, . . .	18.06	17.92 = Sb
Iodine, ...	52.47	52.91 = I_3
	100.00	100.00 = $2\,Zn\,(C_4H_5)\,I + Sb\,(C_4H_5)_3\,I$

which, as will be seen, show that the substance analyzed was a compound of iodide of zincethyle and iodide of stibithyle, and therefore prove that $SbZn_3$ is decomposed even by iodide of ethyle. A similar compound, $Zn\,(C_4H_5)\,I + As\,(C_4H_5)_3\,I$, is described by Cahours and Riche as formed by the action of iodide of ethyle on arsenide of zinc.*

6th. Weak hydrochloric or sulphuric acids decomposed $SbZn_3$ with great violence. Hydrogen gas escaped mixed with only a very small amount of antimoniuretted hydrogen,† the zinc dissolved, and the greater part of the antimony was left behind as a black amorphous powder.

7th. Nitric acid also violently decomposed $SbZn_3$, forming soluble nitrate of zinc, and an insoluble white powder, which was a mixture of basic nitrate of antimony and of antimonious or antimonic acid.

---

* *Compt. Rend.*, June, 1853, p. 1001.

† Lassaigne found that the gas evolved from an alloy of three parts of zinc and two of antimony, when treated with dilute sulphuric acid, contained at most only two per cent of its volume of antimoniuretted hydrogen. *Journal de Chimie Medicale*, Vol. XVII. p. 444, or Berzelius, *Rapport Annuel*, 1842.

8th. Hydrochloric acid mixed with a few drops of nitric acid completely dissolved the compound, and a solution was obtained of chloride of zinc and chloride of antimony, from which the two metals could be precipitated and determined in the usual way.

The most obvious explanation of all these phenomena seems to be, that $SbZn_3$ is a radical in which the affinity between the elements is very feeble. The rapid decomposition of water; the facts that pure hydrogen, and not antimoniuretted hydrogen, is evolved during the process; that rapid decomposition is produced by the alloys of zinc and antimony only when they have the composition of $SbZn_3$; and, finally, that the composition of $SbZn_3$ is similar to that of $SbMe_3$ and $SbAe_3$, zinc, an electro-positive metal, supplying the place of an electro-positive radical, — all point to the conclusion that $SbZn_3$ belongs to the ammonia family. On the other hand, the action of strong chemical agents on the compound proves that the affinity between its elements is very feeble, and that these agents, under ordinary conditions at least, have a stronger affinity for the zinc of the radical than for the radical itself.

Should the opinion here advanced in regard to the nature of $SbZn_3$ be correct, it undoubtedly will be soon substantiated by the examination of other similar compounds of antimony or arsenic. Moreover, it is not impossible that by some indirect process compounds of $SbZn_3$ may yet be prepared, since only the most obvious methods of combining it have been hitherto tried, my attention having been diverted to what I regarded as a more important subject, the variation in the composition of its crystals. This it is the especial object of the present memoir to elucidate, and here the very feebleness of the affinity, which prevented the formation of compounds, has been of the greatest advantage, by increasing the extent of the variation, which otherwise would probably have been confined within such narrow limits that the discovery of the law which it followed would have been impossible. I propose soon to investigate more fully the chemical relations of this peculiar compound, and, should any important results be obtained, they will be communicated in a future paper.

II. *Binantimonide of Zinc, or Stibiobizincyle*, $SbZn_2$.

Crystals of this compound, having almost exactly the same composition as the theoretical $SbZn_2$, can be obtained by melting together 31.5 per cent of zinc and 68.5 per cent of antimony, and crystallizing, with the precautions already described. From 32 per cent of zinc and 68 of antimony smaller isolated crystals are formed, and therefore better adapted for measurement, but they contain an excess of antimony. In their natural state the crystals of $SbZn_2$, like those of $SbZn_3$, have a silver-white color, and a very bright metallic lustre. Their hardness = 3.5. Their specific gravity varies with their composition; that of crystals containing 33.6 per cent of zinc = 6.384. They are frequently perfect, and their faces so plane and bright that the angles can be measured to a minute. Fig. 3 represents an isolated crystal, which was formed in an alloy containing 32.5 per cent of zinc. The angles given at the side of the figure were all obtained by measurement, except that over Y, which measured six minutes more than that required by the other two.

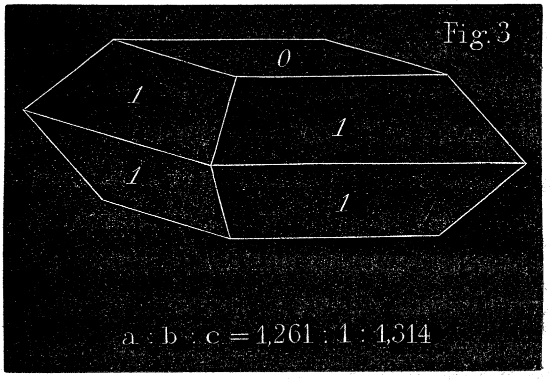


Fig: 3

O on 1 = 122° 15′ measured the same on each side.
1 on 1 over Z = 115° 30′.
1 on 1 over Y = 95° 24′ measured 95° 30′.
1 on 1 over X = 118° 24′.

The isolated crystals of $SbZn_2$, like those of $SbZn_3$, are usually small; but, like the latter, they tend to combine together, with parallel axes, forming large, flat plates. They also frequently unite by a plane parallel to the octohedral face 1, producing a cellular structure which is especially characteristic of the thin plates which form in the alloys between 33 and 43 per cent of zinc. From this it appears that the crystals of $SbZn_2$ differ from those of $SbZn_3$, not simply in their dimensions, but also in their whole character and conformation. Indeed, the difference in this respect could hardly be greater, and will be found to have been of great assistance in the subsequent part of the investigation.

The composition of the crystals of $SbZn_2$ varies with the composition of the alloy in which they form. The three analyses given below, made by Mr. F. H. Storer, are of crystals from three different alloys. No. 1 is the analysis of crystals from the alloy of 31.5 per cent of zinc; No. 2, from the alloy of 29.5 per cent of zinc; No. 3, from the alloy of 27.5 per cent of zinc.

	No. 1.	No. 2.	No. 3.	Calculated.
Zinc, ...	33.95	33.62	33.85	33.55
Antimony, .	66.09	66.38	65.81	66.45
	100.04	100.00	99.66	100.00

These analyses tend to prove that crystals formed in alloys between 27.5 and 31.5 per cent of zinc correspond very closely in composition to the calculated composition of $SbZn_2$.

In its chemical relations $SbZn_2$, unlike $SbZn_3$, is an entirely inactive substance. It does not decompose boiling water except very feebly, and is not attacked by dilute mineral acids. Boiled with strong hydrochloric acid, it is decomposed; but unless reduced to a very fine powder, the decomposition is not complete. Strong nitric acid acts upon it as upon $SbZn_3$, though the first action is less violent.

The Variation in Composition of $SbZn_3$ and $SbZn_2$.

An abstract of the description of the two compounds of zinc and antimony just given was published about a year since in the *American Journal of Science.*[*] It was there stated that crystals of $SbZn_3$ could be obtained, retaining exactly their crystalline form, and yet containing a very much larger amount of zinc than that which corresponds to three equivalents. The important bearing of this fact on many obscure points, both of chemistry and mineralogy, and the circumstance that the large extent of the variation, connected with the fact that the conditions of formation of the crystals were entirely under command, seemed to afford a reasonable prospect of discovering the cause of this remarkable phenomenon, have induced the author to devote the leisure he could spare from his profession during the last year to investigating this subject, and it is the especial object of the present memoir to communicate the results of this investigation. The descriptions of $SbZn_3$ and $SbZn_2$ have been added, in order to make it more complete and more intelligible.

In the course of this investigation crystallizations have been made or attempted of alloys differing in composition by one half to five per cent., according to circumstances, from the alloy containing 95 per cent of zinc to that containing 95 per cent of antimony; but only two crystalline forms were observed, that of $SbZn_3$ and that of $SbZn_2$. Well-defined crystals, like those described under $SbZn_3$, were obtained from the alloys between 43 and 60 per cent of zinc, and even in alloys of a higher zinc percentage crystals of the same form were still seen, although they were no longer well defined.

---

[*] Vol. XVIII. p. 229.

In the alloys between 20 and 33 per cent of zinc, well-defined crystals, like those described under $SbZn_2$, were formed, and finally there separated from the alloys between 33 and 42 per cent of zinc thin metallic plates, which evidently belonged to the same crystalline form. In making the alloys from 43 to 95 per cent of zinc, the zinc was melted first, and when in fusion the antimony added. As the melting point of antimony is much above that of zinc, the fluid zinc acted on the solid antimony as a solvent, dissolving the pure metal, but not the impurity, which rose to the surface, forming a scum. The scum seemed to take with it some of the antimony, and thus caused a loss, which, together with the impurity, was found by experiment to be about three per cent of the antimony used. This resulted in raising the percentage of zinc in the alloy at most about eight tenths of one per cent. The alloys below 43 per cent of zinc were made by melting the antimony first, and then adding the zinc. By this method the loss of antimony was very greatly diminished, and, counting the impurity, was found to be only about one per cent and a half of the antimony used. In preparing the alloys, this loss was always allowed for, and the crystallizations were all made as nearly as possible under the same circumstances, so that any unsuspected cause of error should affect all equally. The crystals formed in the alloys were all analyzed. Several methods for separating zinc and antimony were tried, but the process which finally recommended itself as the most accurate was the following.

Method and Results of Analysis.

From five decigrammes to one gramme of the crystals were dissolved in strong hydrochloric acid, to which had been added about one tenth of nitric acid, and the solution heated until the excess of the latter was expelled. It was then diluted largely with water, which precipitated oxide of antimony; sulphuretted hydrogen was passed through the liquid for at least an hour, and the beaker left standing on the sand-bath until the odor of the gas had disappeared. The precipitate, which was now a mixture of sulphur and of sulphide and a little oxide of antimony, was next collected on a tared filter, and, having been dried at 100° C. and weighed, the amount of antimony which it contained was determined by reducing a portion with hydrogen in the usual way. The loss of antimony in the last step can be almost entirely avoided by making the exit-tube of the bulb, used for reducing the mixed sulphide, very small, and keeping an inch of it red hot during the process, and also by a little practice in regulating the temperature of the bulb and the current of hydrogen so as to drive off all the free sulphur before the sulphide begins to decompose. In order to show how great accuracy may be attained by this method, I will subjoin the results of two reductions of different portions from the same mass of mixed sulphides.

Whole amount of mixed sulphides, 0.8423.

	No. 1.	No. 2.
Weight of reduction tube, ...	4.2793	6.2020
" " " " + ($SbS_3 + SbO_3 + S$),	4.4715	6.4044
" " " " + Sb (after reduction),	4.3920	6.3207
" " ($SbS_3 + SbO_3 + S$), ...	0.1922	0.2024
" " Sb, ...	0.1127	0.1187

$$0.1922 : 0.1127 = 0.8423 : 0.4939 \therefore 0.2024 : 0.1187 = 0.8423 : 0.49397.$$

Several similar examples might be given. The filtrate from the mixed sulphide, containing nothing but zinc in solution, was collected with the washings in a large beaker glass, which was covered with a shallow glass tunnel having the orifice so fine as to allow fluid only to drop. The beaker was heated on a sand-bath, and when the liquid was in ebullition a concentrated solution of carbonate of soda was poured into the tunnel, from which it dropped gradually into the boiling liquid. The zinc was in this way invariably perfectly precipitated, and the carbonate obtained in a granular condition, which rendered the subsequent filtering and washing exceedingly easy. This very simple mode of precipitating zinc must have occurred to others, but as I have never seen it described, I will add, that it is very much to be preferred to the ordinary mode of precipitating in a flask. It renders the determination of zinc one of the most accurate of Analytical Chemistry; in proof of which I would refer to the analyses of crystals from the alloys of 33, 32.5, and 29.5 per cent of zinc, given in the table of analyses on the next page. The only source of error in this process arises from neglecting to wash thoroughly the precipitated carbonate of zinc.

In all the analyses published in this memoir, the zinc was determined by the method just described; but, unfortunately, the accuracy of the method indicated above for determining antimony was not ascertained until the investigation was half finished. In the earlier analyses the antimony was determined from a separate portion of crystals by the method commonly used, namely, dissolving in aqua regia, adding tartaric acid before diluting, in order to keep the oxide of antimony in solution, and determining the sulphur in the precipitated sulphide as sulphate of baryta. This process in the hands of the author proved much less generally accurate than the one which has been recommended; for the slight loss of antimony to which the analyst is liable while reducing with hydrogen was found to be more than counterbalanced by the greater length of the last process, and the danger of obtaining a small amount of oxide mixed with the sulphide. The analyses were all made in my laboratory, under my direction and immediate supervision, and the greater part of them by myself. The rest, with one exception, were made by my assistants, Mr. F. H. Storer and Mr. C. W. Eliot, to whose great care and accuracy I take pleasure in bearing witness. Their work is, in all respects, as reliable as my own. The results are collected in the following table, which will explain itself.

Analyses of the Crystals formed in the Alloys of Zinc and Antimony.

Composition of the Alloys by Synthesis.		Composition of the Crystals by Analysis.			Name of the Analyst.
Per Cent of Zn.	Per Cent of Sb.	Per Cent of Zn.	Per Cent of Sb.	Sum.	
70.40	29.60	64.15	35.77	99.92	Cooke.
66.50	33.50	61.00	39.00	*100.00	"
64.50	35.50	58.50	41.44	99.94	"
60.60	39.40	55.00	45.09	100.09	Homer.
58.60	41.40	50.39	49.29	99.68	Eliot.
56.60	43.40	49.92	50.05	99.97	"
54.70	45.30	48.26	51.42	99.68	Storer.
52.70	47.30	47.47	52.53	†100.00	Cooke.
50.70	49.30	46.89	53.11	†100.00	"
do.	do.	46.45	53.55	†100.00	"
48.70	51.30	48.66	51.34	†100.00	Eliot.
46.70	53.30	46.77	53.23	†100.00	"
44.80	55.20	44.26	55.73	†100.00	"
43.80	56.20	44.04	55.96	†100.00	Cooke.
42.80	58.20	43.15	56.93	100.08	"
do.	do.	43.06	56.50	99.56	"
do.	do.	42.83	57.24	100.07	"
33.00	67.00	35.37	64.57	99.94	"
do.	do.	35.40	64.60	†100.00	"
32.50	67.50	34.62	64.92	99.54	Storer.
do.	do.	34.61	65.39	†100.00	Eliot.
31.50	68.50	33.95	66.09	100.04	Storer.
29.50	70.50	33.62	66.38	†100.00	"
do.	do.	33.62	66.38	†100.00	"
27.50	72.50	33.85	65.81	99.66	"
26.50	73.50	32.08	67.60	99.68	"
26.00	74.00	30.74	69.06	99.80	Cooke.
25.50	74.50	30.43	69.51	99.94	Storer.
25.00	75.00	29.88	70.20	100.08	Cooke.
24.50	75.50	28.76	71.24	100.00	"
23.50	76.50	27.93	71.85	99.78	"
22.50	77.50	26.62	73.27	99.89	Storer.
21.50	78.50	24.83	74.74	99.57	Cooke.
20.12	79.88	20.58	79.42	100.00	"

---

* In this analysis the antimony only was determined.

† In these analyses the zinc only was determined.

Curve of Variation in Composition.

In order to compare together the composition of the crystals and that of the alloy in which they form, I have resorted to the usual method of Analytical Geometry, and in the plate at the end of this memoir the lower horizontal line is the axis of abcissas, and the vertical line at the extreme left the axis of ordinates. The first has been divided into equal parts, which denote the per cents of zinc in the crystals, and the last into parts of the same size, which stand for the per cents of zinc in the alloys. The zinc rather than the antimony determinations have been selected for comparison, as being generally more accurate, and as having been all made in exactly the same way. The points determined by analysis are indicated with dots, and the double line drawn through these dots is a curve, which represents the relation of the composition of the crystals to that of the alloy in which they form. In order to make clear the connection between the two, it will be well to discuss this curve, commencing with what may be termed the two centres of crystallization, the alloys of 42.8 and 31.5 per cent of zinc, and examining the effect produced on the crystals by diminishing or increasing the amount of zinc in the alloy.

It has already been stated, that the crystals of $SbZn_3$ are obtained in their greatest perfection from the alloy of 42.8 per cent of zinc. They are then comparatively large, generally aggregated, and, as the three analyses already cited prove, have the same composition as the alloy. On increasing gradually the amount of zinc in the alloy up to 48.7, the crystals continued to have the composition of the alloy, and the only difference which could be observed in their character was, that they were smaller, and more frequently isolated. Between these limits the whole mass of the alloy exhibited a strong tendency to crystallize, and by pouring it as it cooled from one vessel to another, it could be crystallized to the last drop. The portion *a b* of the curve is therefore a straight line equally inclined to the two axes. On increasing the amount of zinc in the alloy to 50.7 per cent, the amount of zinc found in the crystals was only 46.89 per cent, and above this it was uniformly less than it was in the alloy; but no closer relation between the two could be detected, owing undoubtedly to the unavoidable irregularity in the crystallizations of the alloys which contained more than 50 per cent of zinc. This arose from a peculiar pasty condition which the fluid mass assumed at the point of crystallization, apparently caused by the separation of the excess of zinc. Definite crystals, however, were obtained even from the alloy of 60 per cent of zinc, which contained 55 per cent; above this, the crystals became less and less abundant, and gradually faded out, although the alloy even of 86 per cent of zinc exhibited a radiated crystalline texture, and a trace of this structure could be still discovered even in the alloy containing only 4 per cent of antimony. It might be supposed that, on returning to the alloy of 42.8 per cent of zinc, and increasing the amount of antimony, we should obtain crystals containing an excess of antimony; but so far is this from being true, that the slightest excess of antimony entirely changes the character of the crystallization. On crystallizing an alloy containing 41.8 per cent of zinc, not a trace of any prismatic crystals could be seen, but in their place there was found a confused mass of thin metallic scales, which, as will soon be shown, are imperfect crystals of $SbZn_2$. Thus it appears that, although perfectly formed crystals of $SbZn_3$ can be obtained containing 55 per cent of zinc, they cannot be made to take up the slightest excess of antimony. A more remarkable example of break in continuity than the lower limit of $SbZn_3$ I have never seen. It was brought to notice very forcibly on attempting to recrystallize a quantity of alloy of 42.8 per cent of zinc, which had already afforded large and definite crystals of $SbZn_3$, after adding a very small piece of antimony, when no trace of crystallization could be obtained except the scales described above.

In order to obtain crystals having the composition of $SbZn_2$, that is, containing 33.5 per cent of zinc, it is necessary to crystallize an alloy at least as low as 31.5 per cent of zinc. At this point large compound crystals are obtained corresponding to the large crystals of $SbZn_3$. On increasing the amount of zinc in the alloy up to 33 per cent, the proportion of zinc in the crystals appeared to increase in the same ratio, so that the curve of $SbZn_2$ is, at this part, a straight line parallel to the curve of $SbZn_3$. It should, however, be noticed, that the extent of this line, *k i*, is so limited, that a very small error in the analyses might change very considerably its direction. The crystals of $SbZn_2$, containing an excess of zinc, are smaller and more frequently isolated than those containing exactly two equivalents. A similar fact, it will be remembered, is true of the crystals of $SbZn_3$. At the alloy of 33 per cent of zinc the definite crystals of $SbZn_2$ begin to disappear, and are succeeded by thin metallic scales, which, as the two following facts will prove, are imperfect crystals of the same crystalline form. First, the scales from the alloy of 33 per cent are frequently found having a definite crystal as a nucleus, when it is evident that their surfaces are extensions of the basal plane *O* of Fig. 3. Secondly, the scales twin together like the large tabular crystals of $SbZn_2$, forming a cellular structure; and the angle between two scales thus united measured, with an application goniometer, approximatively 115° 30′, and was therefore equal to the basal angle of the definite crystals. These scales continue up to the alloy of 41.8 per cent of zinc, becoming, however, constantly less abundant and less distinct.

Several specimens of them were analyzed, but no regularity in their composition could be detected, except that they all contained a very much larger amount of zinc than the alloys in which they formed. This irregularity and the imperfection in the crystallization seem to be caused by the interference of $SbZn_3$, that is, by a tendency to form $SbZn_3$, which exhibits itself in a proneness of the crystals of $SbZn_2$ to an excess of zinc. The line *k i* has been continued with dots, in order to show that the influence of $SbZn_2$ extends as far as the alloy of 42.8 per cent of zinc. On returning to the alloy of 31.5 per cent of zinc, and adding an excess of antimony, it was found that the crystals formed continued to have the theoretical composition of $SbZn_2$ until the amount of zinc in the alloy had fallen to 27 per cent, so that the tendency towards the theoretical composition was so great, that in the alloys between 31.5 and 27 per cent of zinc, crystals were formed having very nearly this composition. On still further increasing the amount of antimony in the alloy, the composition of the crystals gradually approached that of the alloy, and from the alloy of 20.2 per cent of zinc very imperfect crystals were obtained, having almost the same composition as the menstruum. At the same time the crystals became less and less perfect, and finally disappeared altogether in the alloys below 20 per cent of zinc.

The portion of the curve *k m n h* is the most important result of this investigation, and therefore deserves especial notice. It has been shown that crystals of the form of $SbZn_2$, or at least crystalline scales of the same character, are formed in the alloys between 20 and 43 per cent of zinc, the first per cent corresponding to SbZn, and the second to $SbZn_3$. Half-way between these two points, that is, the alloy of 31.5 per cent, is the point where crystals having the calculated composition of $SbZn_2$ are first obtained. Were the variation in the composition of the crystals of $SbZn_2$ exactly proportional to the excess of zinc or of antimony in the alloy, as is the case with $SbZn_3$, then the curve of variation would be the straight line formed by the continuation of the line *a b*. From this line (*b h*) the course of the curve is deflected by the force which determines the union of the elements in definite proportions, and which, for the want of a special term, I will call the Chemical Force. This is so strong, that the curve runs parallel to the axis of ordinates through the distance *k m*. Beyond this point the influence of the excess of antimony in the alloy becomes stronger than the chemical force, and the curve gradually bends towards the line *h b*, which it finally meets at *h*. In the portion *h n* of the curve the analyses are best represented by the arc of a circle, of which the radius equals *h e*, one half of *h b*, and to which the line *k m* is tangent. In the portion *n m* the points determined by analysis may also be connected by the arc of a circle, of which the radius *o′ n* equals the difference between the radius *o n* and twice *g n*, so that the two centres are at the same distance from the line *a h*. The whole curve is evidently the result of two forces; one acting along the chord in the direction *b h*, a force tending to increase the amount of antimony in the crystals proportional to the amount in the alloy, the same force in fact which acts undisturbed in forming the portion of the curve *b a ;* the other, the chemical force acting in the direction of the tangent *k m*. It has already been stated, that crystals having the calculated composition of $SbZn_2$ are not first formed in the alloy of the same composition, 33.5 per cent of zinc, but in an alloy containing two per cent less; so that the line *m k*, instead of extending to *e*, diverges from this direction at *k*, and afterwards runs parallel to the line *b h*. Unless this fact can be explained by a tendency in $SbZn_2$ to an excess of zinc caused by the influence of $SbZn_3$, as suggested above, the reason of the difference between $SbZn_2$ and $SbZn_3$ in this respect is not clear; but as some evidence that it is not accidental, it may be stated that the distance *k c* equals *c i*, the last point being the one at which the tangent line *m k* extended meets the curve. Another remarkable fact, whose bearing cannot at present be seen, but which, like the last, serves to corroborate the general accuracy of the result, was pointed out by my friend and colleague, Professor Peirce, after the plate had been engraved. The distances of the three most important points of the curve of $SbZn_2$ from the line *a h*, namely, *k d*, *m f*, and *n g*, are simple multiples of the first; *n g* is twice and *m f* three times *k d*. The curve has been fixed, as will be noticed from the dots, by a large number of points determined throughout the greater part of its length at every per cent, and in the portion *m n* at every half per cent. They certainly coincide with the curve as closely as could possibly be expected, and the very agreement of so many different determinations by three separate analysts is a strong proof of the general correctness of the work.

By making hypotheses in regard to the nature of the two forces which have generated the curve just described, it would not be difficult to obtain for it a mathematical expression; but as such hypotheses in our ignorance of the nature of these forces would be premature, I must content myself with giving its geometrical construction on a chart, ruled like the plate at the end of the memoir. Let the co-ordinates of any point of the curve be $x =$ per cent of zinc in the crystals, and $y =$ per cent of zinc in the alloy. In order to construct the curve of $SbZn_3$, find a point (*a*) of which $x = y = 43$ per cent (the calculated per cent of $SbZn_3$), and draw a straight line *a b* equally inclined to the two axes in the direction from the origin. To construct the curve of $SbZn_2$, produce the line *a b* in the opposite direction to the point $x = y = 20$, which will be the lowest point of the curve. Find next a point (*k*) of which $x = 33.7$ per cent (the calculated per cent of $SbZn_2$ is 33.5), and $y = 31.5$ per cent, which is one half of $43 + 20$. Through this point draw a line $m\ k$, parallel to the axis of ordinates, and intersecting the line $a\ b\ h$ at c. The line $m\ i$ is the tangent, and the line $b\ h$ the chord, of the required arc. On the line $m\ i$ take $c\ i = c\ k$, and i is the point at which the arc should touch the tangent. Erect a perpendicular on the tangent at the point i; take $o\ i =$ half $b\ h$, and from o as a centre with a radius $= o\ i$ describe the arc $h\ n\ i$. Also, from the centre o let fall a perpendicular $o\ g$ on the chord $b\ h$, and produce it to a point o', making $o'\ g = o\ g$. It will intersect the arc at n. From o', as a centre with a radius $o'\ n$, describe a second arc, $m\ n$ intersecting the tangent at m. Finally, draw from k a straight line $k\ l$ parallel to $b\ h$, then the broken line $l\ k\ m\ n\ h$ will be the required curve.

It will be noticed that the tangent, which has been laid down on the plate through the points determined by analysis, is two tenths of one per cent in advance of the line which would correspond to $SbZn_2$. This position is essential to the equality of $k\ c$ and $c\ i$, if we retain as the value of the radius of the larger arc $R = \frac{1}{2}\ b\ h$. If the analyses should have given erroneously too much zinc, so that the true position of the line should be at $x = 33.5$ per cent, then this equality would be destroyed, and the conditions for finding the centre o would be reduced to the co-ordinates of the point h, the length of the radius, and the position of the tangent, from which, by a very simple construction, the curve might be drawn. It should, however, be remarked, that the position of the tangent in advance of the line $x = 33.5$ is in accordance with the fact, already noticed, that the crystals of $SbZn_2$ have, throughout, a proneness to an excess of zinc, caused apparently by the influence of $SbZn_3$; but it is also true that the tendency of the error in the zinc determinations is in the same direction.

Before discussing the conclusions to which the facts already stated seem directly to point, it will be well to see how far the variation in composition corresponds to a variation in the properties of the two compounds. Three classes of properties have been examined in this connection; namely, Specific Gravity, Crystalline Form, and Affinity for Oxygen, which will be treated of in order.

Specific Gravity.

The specific gravity of all the crystals analyzed, as well as that of the antimony and zinc used in the investigation, has been taken with the greatest care. The determinations were made with a nicely constructed specific gravity bottle, as this method was found susceptible of greater accuracy than any other when the temperature of the water was observed with precision. The small double cone of silver recommended by

Scheerer * was tried, but so great accuracy could not be obtained with it as with a bottle.† On an average, about ten grammes of crystals ‡ were taken for each determination, and the bottle used was capable of containing about the same weight of water. The crystals, coarsely powdered, were introduced into the bottle, covered with water, and, on account of the action of $SbZn_3$ on hot water, the entangled air was removed by an air-pump. The bottle was then filled with water, and, after the stopper had been introduced, suspended in a large beaker of water, the temperature of which was very slightly higher than that of the room. In contact with it was placed the bulb of a centigrade thermometer, graduated to tenths of a degree. When an equilibrium had been established in the temperature, the bottle was removed from the beaker, wiped dry, and weighed. In calculating the specific gravity the weight of the water was corrected for the temperature so that the unit is in all cases distilled water at 4° C. A similar correction could not be made for the temperature of the substance, as the coefficients of expansion of the crystals are not known; but as the maximum difference between the temperatures in the different determinations was not over 10° C., this correction would only very slightly affect the relative results. The mean temperature was about 15° C. In order to show that very accurate results can be obtained by delicate manipulation with a specific-gravity bottle, I will subjoin the numbers obtained in the determination of the specific gravity of antimony and zinc.

---

* Poggendorf, *Annalen*, Vol. LXVII. p. 120.

† A specific-gravity bottle for delicate experiments should be made with a thick rim, ground square at the top, and the glass stopper should be so fitted to the neck as not to leave a channel between the two in which water can collect.

‡ The very great liability to error which the use of a small amount of substance, in a specific gravity determination, necessarily involves, does not seem to be appreciated by many experimenters, and it may therefore be of use to add a very simple mathematical statement of the process. Let M = weight of substance at 4° C. and m = weight of bottle filled with water at same temperature. Place x = the weight of bottle, substance, and water, as this is the weight on which the accuracy of each determination depends, since the weight m is the same for all, and is the mean of a large number of observations; then Sp. Gr. = $\frac{M}{(M+m)-x} = u$; $\delta u = \frac{u^2}{M}\delta x$. Here δu represents the amount of error produced in the specific gravity by making an error of δx in the weight. Suppose $u = 6.32$, then $\delta u = \frac{40}{M}\delta x$, so that, if forty grammes of the substances are used, an error of one millegramme in the weight x will produce an error of one one-thousandth in the specific gravity. Suppose, however, only one gramme is taken, then the same error in the weight x will cause an error of four one-hundredths in the specific gravity. From this it appears, that, where only a limited amount of a substance is at command, it is best to unite it all in one careful experiment, rather than to distribute it through several; for it must be remembered, that, of two experiments in which the liability to error is as one to four, the relative value is not as these numbers, but as their squares.

	1.	2.
Weight of antimony,	18.8642	12.5433
" " water displaced at 4° C.,	2.8250	1.8785
Specific gravity of antimony at 15° compared with water at 4°,	6.677	6.677

	1.	2.
Weight of zinc,	12.4145	11.0383
" " water displaced at 4° C.,	1.7356	1.5431
Specific gravity of zinc at 12°.4 C. compared with water at 4°,	7.153	7.153

In the table on the opposite page, the results of the specific gravity determinations are given in the column headed "Sp. Gr. of Crystals by Experiment." Each number is the mean of at least two, and generally of three experiments, agreeing within a few thousandths. The column headed "Mean Sp. Gr. of Zinc and Antimony," is the calculated specific gravity of the same crystals, on the supposition that the two metals had undergone no expansion on uniting. The last column gives the differences of these two numbers, and therefore shows the amount of expansion. On examining the table it will be found, — 1st. That the union of antimony and zinc is accompanied with expansion; 2d. That the specific gravity of the crystals varies slightly with the composition; 3d. That the two minimum specific gravities correspond precisely to the composition of $SbZn_2$ and $SbZn_3$, so that the specific gravity increases, and the expansion diminishes, as you depart on either side from these two centres; 4th. That the specific gravity of $SbZn_3$ is smaller than that of $SbZn_2$. We find, then, that the specific gravity determinations confirm, in general, the results of the analyses, pointing out the same two centres of crystallization.

Crystalline Form.

It has already been stated, that only two crystalline forms can be obtained from the alloys of zinc and antimony, — that of $SbZn_3$ and that of $SbZn_2$. A large number of crystals of $SbZn_3$ from different alloys, and therefore containing different proportions of zinc, were carefully measured for the purpose of ascertaining whether the angle was at all affected by the variation of composition. Fortunately, four different crystallizations afforded excellent crystals, the angles of which could be measured to a minute. The crystals contained, respectively, 43.15, 44.14, 46.90, and 55.00 per cent of zinc, and on all these, by repeated measurements, the angles were found to be *identical* with those given under Figs. 1 and 2. Crystals from many of the other alloys were also measured, but on account of the imperfections of their surfaces the angles could not be

Specific Gravities of Crystals formed in the Alloys of Zinc and Antimony.

Composition of the Alloys.		Composition of the Crystals.		Sp. Gr. of Crystals by Experiment.	Mean Sp. Gr. of Zinc and Antimony.	Expansion in Crystallizing.
Per Cent of Zn.	Per Cent of Sb.	Per Cent of Zn.	Per Cent of Sb.			
100.00				7.153	7.153	0.000
*96.00	4.00			7.069	7.134	0.065
*86.20	13.80			6.898	7.086	0.188
*76.30	23.70			6.769	7.039	0.270
70.40	29.60	64.20	35.80	6.699	6.982	0.283
66.50	33.50	61.00	39.00	6.628	6.967	0.339
64.50	35.50	58.56	41.44	6.596	6.956	0.360
62.50	37.50	55.53	44.47	6.506	6.941	0.435
60.60	39.40	55.00	45.00	6.440	6.939	0.499
58.60	41.40	50.39	49.61	6.396	6.917	0.521
56.60	43.40	49.95	50.05	6.388	6.915	0.527
48.70	51.30	48.66	51.34	6.404	6.909	0.505
46.70	53.30	46.77	53.23	6.376	6.900	0.524
44.80	55.20	44.26	55.74	6.341	6.888	0.547
42.80	57.20	43.09	56.91	6.327	6.882	0.555
*40.00	60.00			6.386	6.867	0.481
*35.00	65.00			6.404	6.844	0.440
33.00	67.00	35.37	64.63	6.401	6.845	0.444
29.50	70.50	33.62	66.38	6.384	6.837	0.453
27.50	72.50	33.85	66.15	6.383	6.838	0.455
26.50	73.50	32.08	67.92	6.400	6.829	0.429
26.00	74.00	31.07	68.93	6.418	6.824	0.406
25.50	74.50	30.43	69.57	6.428	6.822	0.394
24.50	75.50	28.76	71.24	6.449	6.813	0.364
22.50	77.50	26.62	73.38	6.453	6.803	0.350
21.50	78.50	24.83	75.17	6.467	6.795	0.328
*15.00	85.00			6.564	6.748	0.184
*10.00	90.00			6.603	6.725	0.122
*5.00	95.00			6.655	6.701	0.046
	100.00			6.677	6.677	0.000

* Alloys not crystallized.

determined within five or ten minutes. In all these cases, however, the values of the angles given above were included within the limits of uncertainty.

The faces of the crystals of $SbZn_2$ are not generally so perfect as those of $SbZn_3$, nor is their tabular form so well adapted for measurement. Moreover, variations in some of the angles have been noticed in crystals from the same crystallization, amounting even to ten minutes. The angle *O* on 1, however, appeared to be very constant, for in all cases where it could be accurately measured the same value was obtained. As none of the crystals of $SbZn_2$, containing an excess of antimony, could be measured with precision, no constant variation of angle could be detected, and, on the other hand, it could not be proved to be invariable.

Affinity for Oxygen.

The affinity of the crystals of $SbZn_3$ of different compositions for oxygen was estimated by boiling alloys of the same composition as the crystals with water, and measuring the amount of hydrogen evolved in a given time. The following table contains the results of these experiments. Column 1 gives the number of cubic centimetres of hydrogen obtained by boiling 200 grammes of different alloys (granulated) with water. The per cent of zinc contained in the alloys is given at the left-hand side of the table, opposite to the number of cubic centimetres. The composition is known only synthetically. The alloys were made by melting together the zinc and antimony of commerce in the required proportions, making no allowance for impurities, and when melted, they were granulated as nearly as possible under the same conditions. Two hundred grammes of each alloy were boiled with water, the gas collected over water, and the number of cubic centimetres evolved in an observed time read off after the gas had been cooled to 20° C. These amounts were afterwards reduced for ten minutes, and, thus reduced, are given in the table. As it was impossible to obtain granules of a uniform size in all the alloys, another set of experiments was made in a precisely similar way, except that the alloys were cast into small cylinders of a uniform size. As these cylinders had absolutely the same diameter, and very nearly the same specific gravity, throughout, the same amount of surface was obtained by weighing out 200 grammes of each alloy, and taking care to have the same number of little cylinders in each lot. Column 3 gives the results of these experiments. It will be seen that the two sets of numbers compare as closely as could be expected, it being remembered that the amount of surface in the first set of experiments was variable, while that in the second was constant, and smaller than the first. These results, however, are only approximate. The limits of variation in different experiments on the same alloy would quite cover the differences between the first ten numbers of column 1, excepting the first, so difficult is it to granulate the alloys to a uniform size, and submit them during the experiments to precisely similar conditions. The numbers of column 3, from which the variations due to difference of surface have been eliminated, are probably, relatively to each other, very nearly correct.

Table of the Amounts of Hydrogen Gas evolved by 200 *Grammes of Different Alloys of Antimony and Zinc, in Ten Minutes, at* 100° *C. measured at about* 20° *C.*

Per Cent of Sb.	1.	2.	3.
0	2	63	
5	6	34	
10	4	28	3
15	4		
20	6	18	5
25	4	19	
30	4	31	5
35	5	49	
40	6	72	7
45	5	45	
50	8	44	9
55	17	46	
58	130	244	84
60	50	139	47
65	14	35	
70	10	45	7
75	6	36	
80	5	23	6
85	4	20	

A mere glance at the table will discover two facts: —

1st. That up to 40 per cent no great increase in the amount of hydrogen evolved is obtained by increasing the amount of zinc in the alloy.

2d. That at the alloy containing 42 per cent of zinc there is an immense maximum, which is confined at most between two per cent on either side.

It is a well-known fact, that the rapidity of the evolution of hydrogen from dilute sulphuric acid and zinc can be very greatly increased by adding to the materials a few drops of a solution of bichloride of platinum. The platinum, being immediately deposited over the zinc, forms with it a galvanic pair, and thus increases the affinity of the zinc for oxygen. The same increased action can be produced by the same means in the decomposition of pure water by the antimony and zinc alloys. Column 2 of the table gives the results which were obtained by boiling with pure water in a small flask 200 grammes of the granulated alloys previously treated, with the same amount in each case of a solution of chloride of platinum. After the platinum had been deposited on the granules, and the surfaces had been thus blackened, the alloys were thoroughly washed with water, and the experiments conducted as in the other two cases. These experiments were made with the same alloys as those from which the numbers of column 1 were obtained. As, however, in the experiments with bichloride of platinum, new and obvious causes of irregularity were introduced, that did not exist in the other two sets of experiments, no great uniformity can be expected on comparing the results. The two main facts, however, noticed in the columns 1 and 3 of the table, are quite as prominent in column 2, and also the additional fact that the presence of platinum very greatly increases the rapidity of the evolution of hydrogen from the alloys.

One set of results given in the table requires particular notice, — those obtained from *pure* zinc, to be found on the first line opposite 0 per cent of antimony. It is stated with great confidence, by all chemical authors* who have written on the subject, that zinc does not decompose water at the boiling temperature. On this account the experiments with pure zinc were made with peculiar care, and repeated several times, great pains being taken to insure that both the zinc and water employed were perfectly pure. There is no doubt in regard to the fact of the decomposition, which becomes, as is shown in the table, quite rapid when the affinity of the zinc is strengthened by the galvanic action of the platinum.

It has already been shown, that, when the alloys of zinc and antimony are treated with hydrochloric or sulphuric acid, they are, as a general rule, and under favorable circumstances, completely decomposed, the zinc uniting with the acid, and the greater part of the antimony separating as a black powder, only a very small amount ever, even under the most favorable circumstances, escaping as antimoniuretted hydrogen. When the alloys are in granules, it is almost invariably the case with those containing more than 50 per cent of antimony, that after a short time the acid ceases to act, owing to the formation of a coating of antimony on the surface. The action is, of course, renewed on reducing the alloy to powder, but here, as in other alloys, the less oxidizable metal appears to be able to protect entirely a certain amount of the other from the action of acids.

These facts, in connection with those previously stated in regard to the increased action of the alloys on water in presence of platinum, sufficiently explain the remarkably rapid decomposition of water obtained by means of alloys which have been previously acted upon by dilute hydrochloric or sulphuric acids, even after the excess of acid and the salts formed have been completely removed by repeated washings. This decomposition is so rapid, that I have obtained from 200 grammes of an alloy containing 43 per cent of zinc, prepared as just described and boiled with water, nearly a litre of gas in ten minutes. It is plain that the antimony acts here exactly as the platinum in the previous experiments, by forming a galvanic circuit with the alloy. A set of experiments was made with alloys, which had been acted upon by acids, similar to those the results of which are given in the table. The irregularities, however, which resulted from the unequal action of the acids on the different alloys, from the differences of surface, and from other causes, rendered the final results so discordant, that they were of no value for comparison. They were always much greater than those obtained by using platinum, with the exception of pure zinc, whose decomposing power was not increased by the action of acids.

---

* Since this was written, and first published in the *American Journal of Science* for September, 1854, I find that Deville has noticed the fact of the decomposition of boiling water by zinc. *Comptes Rendus*, 14 Aout, 1854, p. 322, note.

This new mode of decomposing water is of value as a process for preparing pure hydrogen, and also for illustrating the composition of water to a class. My mode of preparing the alloy for making pure hydrogen is simply thus. I melt together equal parts of zinc and antimony free from arsenic (this alloy being nearly as active after having been treated with acid as the alloy of 43 per cent of zinc), and granulate as finely as possible. I place the granules in a deep porcelain basin, and pour over them enough hydrochloric acid of ordinary strength to cover them. An energetic action ensues, which I allow to continue until it becomes weak, and the acid nearly exhausted. The excess of acid, and also the chloride of zinc formed, I now wash away by allowing a stream of water to pour into the basin until it runs off clear and tasteless. The alloy thus prepared is ready for use. It will evolve hydrogen from boiling water with almost as much rapidity as zinc and dilute sulphuric acid, and even after the temperature of the water has fallen to that of the air, the evolution continues, though only very slowly. A flask containing about 500 grammes of the prepared alloy covered with water continued to evolve hydrogen during the winter for over two months, when the temperature was seldom above 4° C.

The rapidity of the evolution of hydrogen from the alloy and boiling water diminishes quite rapidly, and finally, after several hours, ceases altogether, from the formation of a coating of oxide on the surfaces. The activity can be restored by dissolving off this coating with dilute acids. Where, however, the alloys contain a large per cent of antimony (above 50), the activity cannot be renewed indefinitely in this way, since the particles of antimony set free by the acid adhere to the surface of the alloy, and soon form a coating impregnable to the strongest acid. As has been shown in the previous part of this memoir, when the antimony and zinc used are free from arsenic, the hydrogen obtained by this process is chemically pure. It is, consequently, completely destitute of odor.

General Conclusions.

I stated at the commencement of this memoir, that I expected to be able to prove, first, that zinc and antimony form with each other two, and probably only two, definite compounds; second, that these compounds are capable of a very large variation in composition without any change in the crystalline form; and, lastly, that this variation can only be explained by admitting an actual perturbation in the law of definite proportions produced by the influence of mass. That zinc and antimony form with each other two compounds, and that these compounds are capable of a very large variation in composition without any change in the crystalline form, have been shown to be facts. The cause of this variation can only be inferred. Before stating the conclusions to which, as I think, the facts now established directly point, it will be well to consider the only two admitted principles of chemical science which could possibly be brought forward to explain similar variations. They are, first, that of impurities in crystals; second, that of isomorphous mixtures. It will not be difficult to show that the variations in composition of $SbZn_2$ and $SbZn_3$ cannot be explained by either of these principles.

It is a well-known fact, that crystals frequently take up impurities, which are either dissolved or mechanically suspended in the menstruum in which they form, and it might be supposed, at first sight, that the excess of zinc or antimony in $SbZn_3$ or $SbZn_2$ bore the same relation to their crystals that the sand does to the rhombohedrons of Calcite from Fontainebleau, or oxide of iron and Chlorite to crystals of Quartz; but, in the first place, in all cases where a considerable amount of impurity is present, the crystals are either imperfect, or else the angle is considerably changed, at times even as much as two or three degrees; and, secondly, as such impurities are merely mechanical, the amount in the crystals would in all probability be proportional to the amount present in the menstruum at the time of their formation. Now, in the crystals of $SbZn_3$ from the alloy of 60 per cent of zinc, there is present an excess of zinc amounting to 15 per cent, and nevertheless the crystals are perfect, and their angles identical with those of the crystals obtained from the alloy of 43 per cent. In the crystals of $SbZn_3$ the excess of zinc is, to a certain limit, directly proportional to the excess in the alloy; but in those of $SbZn_2$ the excess of antimony is far from obeying this rule, and were the excess in both cases a mechanical mixture, the variation in both cases would undoubtedly follow the same law. Again, the crystals of $SbZn_3$ take up an excess of zinc, but do not take up an excess of antimony, while those of $SbZn_2$ crystallize with an excess of either, facts which are as inconsistent with the idea of mechanical impurity as the last. Finally, the form of the curve of $SbZn_2$ of itself alone proves that the excess of antimony in the crystals is not in the condition of mechanical impurity, for in that case the variation of composition would not be influenced, as the curve shows that it is, by the chemical force.

A theory that the variation in composition resulted from the mixture of two or more isomorphous compounds, would be even less tenable than the one just discussed, for, in the first place, it would be necessary to assume the existence of two other compounds of zinc and antimony isomorphous with $SbZn_2$, and of one other, if not of more, isomorphous with $SbZn_3$. Not only would such an assumption be contrary to all the analogies of chemistry, and therefore require strong evidence to sustain it; but, in the second place, it can almost be demonstrated that no such compounds exist. The crystals having the calculated composition of either $SbZn_3$ or $SbZn_2$ are marked, as has been shown, by striking peculiarities, and, with one possible exception, similar peculiarities were not observed throughout the whole series of crystals which have been examined. The crystals containing 50 per cent of zinc and of the composition of $SbZn_4$, were found to have a slightly smaller Sp. Gr. than those just above or just below them; but the difference is so small that it may be accidental, and as the crystals exhibited none of the other peculiarities which characterize crystals having the calculated composition of $SbZn_3$ or $SbZn_2$, I could not attach sufficient weight to the one circumstance to feel authorized in admitting a third compound of zinc and antimony. Admitting, however, the existence of $SbZn_4$, yet, as exactly the same angle has been observed on crystals containing 55 per cent as on those containing 43 per cent of zinc, it would be necessary, in order to explain the variation in composition by the principle of isomorphous mixtures, to assume the existence of still a third compound isomorphous with $SbZn_3$, and containing more zinc than $SbZn_4$, which would increase greatly the improbability of the theory in question. Again, the only probable compound of zinc and antimony containing less zinc than $SbZn_2$ would be $SbZn$; and it will be remembered that the crystals of $SbZn_2$ which contained the largest excess of antimony corresponded very nearly to this compound. In like manner the crystals of $SbZn_2$ which contained the largest excess of zinc corresponded very nearly to $SbZn_3$. If, then, the excess of antimony or zinc in the crystals of $SbZn_2$ arises from a mixture of isomorphous compounds, it must be that $SbZn_3$, $SbZn_2$, and $SbZn$ are isomorphous. That the first two are not isomorphous may be seen by turning back to the description of their crystalline form, and that there is no crystalline compound $SbZn$ is sufficiently proved by the fact that the crystals of $SbZn_2$, which correspond most closely to it, are so very imperfect, that they would hardly be recognized as crystals did they not form the lower limit of a series. Several other facts pointing in the same direction might be added, but sufficient, it is thought, has been said to show that the variations of composition described in this paper cannot be explained either by mechanical impurities in the crystals or by the mixture of isomorphous compounds.

In the absence of any known principle of chemical science by which the remarkable variations of composition that have been demonstrated in this memoir can be explained, the conclusion is almost forced upon us, that zinc and antimony are capable of uniting and producing definite crystalline forms in other proportions than those of their chemical equivalents; in other words, that the law of definite proportions is not so absolute as has been hitherto supposed. The explanation, then, of the variation of composition which I would offer is, that it is due to an actual perturbation of the law of definite proportions produced by the influence of mass. I suppose, for example, that in the crystals of $SbZn_3$ containing 55 per cent of zinc, the zinc and antimony are united in exactly the same way as in those containing 43 per cent, or, in other words, just as if the equivalent of zinc were increased to 52.57, that of antimony remaining the same. In support of this position I would offer two considerations. The first is, that, if the variation is not caused by mechanical impurities or by the mixture of isomorphous compounds, we can conceive of no other explanation for the phenomenon than the one offered. This, of course, is merely negative evidence, for although science as yet presents us with no principle for explaining variations of composition other than those which have been discussed, and although we can conceive of none others, it does not follow that others may not exist, or may not hereafter be discovered; but, nevertheless, this consideration is important, inasmuch as it meets an obvious objection, which would be urged against any new doctrine which conflicts with a generally received canon of chemical philosophy. The second consideration has the character of demonstration. It is that the curve of variation is evidently generated by a second force counteracting directly the chemical force. This second force, as has been shown, is exerted by the excess of one or the other elements present in the menstruum, and it may therefore be appropriately termed the force of mass. While the chemical force tends to make the curve a straight line parallel to the axis of ordinates, the force of mass would reduce it to a straight line, making an angle of 45° with the axis. Under the influence of both these forces, it follows the arc of a circle between the two. Now, I urge that the character of this curve proves that the chemical force has been directly influenced by what we have called the force of mass, in the same way that the irregularities of the orbits of the planets prove that the force of gravitation exerted by the sun has been disturbed in its action by the influence of the other members of the system. As the details in the form of the curve have been fully discussed in the previous part of the memoir, it does not seem to be necessary to dwell upon this argument, and I would therefore, without further comment, offer the curve as it has been laid down on the plate, as the proof of the validity of the explanation of the variation in composition here advanced.

It is worthy of remark, that, while the curve of variation may be said almost to demonstrate that the law of definite proportions may be disturbed in its action, it also most clearly sustains the integrity of the law itself; for, as may be seen on inspection, the chemical force is sufficiently strong to retain the curve of $SbZn_2$ parallel to the axis of ordinates through a variation in the menstruum of nearly five per cent, and it is only when the excess of antimony present in the alloy exceeds six per cent that the force which it exerts becomes strong enough to disturb the action of the law. What the nature of the disturbing force is must be for the present a matter of theory. I am inclined to believe that it is a phase of the chemical force itself, in the same way that the perturbations in the motions of the planets are a secondary result of the force of gravitation.

Accepting the view of the subject which has been offered, it will be obvious that the very large extent of the variation in the compounds of zinc and antimony is due to the very weak affinity between these elements. Were the chemical force stronger in proportion to the disturbing force, the variation would be lessened; were it weaker, the variation would be increased. This is illustrated in the difference between the curve of $SbZn_2$ and that of $SbZn_3$. It is evident from the action of chemical agents on the two compounds, that one equivalent of antimony and two of zinc are united by a stronger force than one equivalent of antimony and three of zinc, and we find that the crystals of $SbZn_2$ retain the calculated composition under a considerable variation in the composition of the menstruum, while the composition of those of $SbZn_3$ vary with the slightest increase of the amount of zinc in the alloy.

To what extent this perturbation of the law of definite proportions prevails among chemical compounds, it must remain for future investigation to determine. There are, however, a number of facts which tend to prove that it is very general wherever chemical affinity is weak. Four of these I will cite, as being remarkably analogous to the facts under discussion.

1. Rieffel, to whose investigation of the compounds of tin and copper we have already referred, says, after the paragraph quoted in the introduction to this memoir: — " Les aiguilles de $CuSn_{24}$ sont plus grosses que celles de $CuSn_{48}$. On croit, sans oser

l'affirmer, qu'elles sont, par compensation, en nombre moindre, et que des différences analogues ont lieu dans les autres $CnSn_{\phi}$ à mesure que ϕ augmente jusqu'à $\phi = \infty$, ou jusqu'à l'étain pur." It will be noticed that the difference between these needles is precisely the same as the difference between the crystals of $SbZn_3$ containing a small and a large amount of zinc, and I think that no one, after reading Rieffel's paper, can doubt that the compounds of copper or tin vary in composition like those of zinc and antimony.

2. The mineral Discrasite, a compound of silver and antimony, crystallizes in trimetric prisms, of which I on I = 119° 59′.* The analyses given below are copied from Dana's *System of Mineralogy*, changing slightly the order.

$SbAg_3$ = Antimony 28.5, Silver 71.5 = 100. $SbAg_4$ = Antimony 23, Silver 77 = 100.

1.	Andreasberg (foliated granular)	Antimony	24.25	Silver	75.25	= 99.5.	Abich.
2.	Wolfach (coarse granular)	"	24.00	"	76.00	= 100.	Klaproth.
3.	Andreasberg (foliated granular)	"	23.00	"	77.00	= 100.	"
4.	" " "	"	22.00	"	78.00	= 100.	Vauquelin.
5.	Wolfach (fine granular)	"	16.00	"	84.00	= 100.	Klaproth.

It needs no comment on these results to show that discrasite is homeomorphous with $SbZn_3$, and varies like it in composition.

3. In a paper recently published,† W. Satorius von Walterhausen, gives descriptions and three analyses of a new mineral occurring with Dufrenoysite in the Binnen-Valley, Switzerland, in Dolomite. As the analyses do not agree with each other and do not correspond to a simple formula, von Walterhausen regards the compound as consisting of two hypothetical isomorphous compounds, $PbS + AsS_3$ and $2\ PbS + AsS_3$, and calculates the proportions in which these compounds are mixed in the specimens analyzed. He infers that they are isomorphous, from their analogy in composition to Zinkenite and Heteromorphite, $PbS + SbS_3$ and $2\ PbS + SbS_3$, which he regards as isomorphous. Dr. J. D. Dana questions the isomorphism of the last, and thinks that the hypothesis that the new compounds are isomorphous requires further evidence.‡

4. It is stated by Staedeler,§ that crystals of the compound of grape-sugar and common salt can be obtained containing for every equivalent of grape-sugar one or two

---

* Dana's *System of Mineralogy*, 4th ed., Vol. II. p. 35.

† Poggendorf, *Annalen*, Vol. XCIV. p. 123.

‡ *American Journal of Science*, Vol. XIX. p. 355.

§ *Chemical Gazette*, Vol. XIII. p. 44.

equivalents of chloride of sodium, and also of intermediate composition. He states, moreover, that "Calloud, who first observed that the grape-sugar of honey combined with chloride of sodium, found that the amount of the latter varied between 8.3 and 25 per cent." Staedeler refers the variation in composition to a mixture of the compound of one with the compound of two equivalents of chloride of sodium, which he assumes to be isomorphous. He adds, that it may be caused by "inclosed crystals of chloride of sodium, although the eye could not distinguish any heterogeneous constituents."

All the above compounds are examples of weak chemical affinity, accompanied by large variations in composition without any change in the general crystalline form. It is not meant to assert that the variations are identical in character with those of $SbZn_3$ and $SbZn_2$, but only that there is a strong probability that this is the case, which, in the first two instances, amounts almost to a certainty.

If variations in composition of such magnitude are possible when the force of chemical affinity is weak, it is highly probable that some variation may occur when the force is strong; and, whatever view may be taken of the cause of the variation, it will now become a matter of importance to ascertain whether many discrepancies in analyses hitherto referred to imperfections in the process may not be owing to the same cause which influences the composition of the crystals of the two compounds of zinc and antimony. For this purpose it will be best to make several analyses of the same compound, prepared under circumstances differing as widely as possible, and then to apply to the results Peirce's "Criterion for the Rejection of Doubtful Observations." Such investigations will be greatly simplified by the tables prepared by Dr. B. A. Gould, Jr., for facilitating the application of this criterion, to which I would refer all chemists who are inclined to take up this line of investigation.

I am well aware that, in announcing the existence of perturbations of the law of definite proportions, I am calling in question one of the most fundamental dogmas of chemical philosophy, and that the new doctrine will have to encounter prejudice on this very ground. This law is so intimately associated in many minds with the atomic theory, that to such absolute definiteness seems to be its essential characteristic. Nevertheless, I cannot but believe that, laying aside the prejudices which the theory begets, it will be seen by all that the analogies of nature support the doctrine of variation as maintained in this memoir. The phenomena of none of the phenomenal laws* of nature have that definiteness of character which is claimed for those of the chemical law. The planetary orbits are not perfect ellipses. The ratios of the harmonic scale are but approximatively realized. The arrangement of leaves on the stem is not perfectly regular. Isomorphism is seldom absolute. In all we observe only a tendency towards a maximum effect, which is the perfect expression of the law, but which is rarely fully reached. The limits of variation are broader in some instances than in others, but we find no case in which there is absolutely none. This same character, which pervades the other phenomenal laws of nature, I claim for the great law of Chemistry. The definite proportion I regard as a maximum towards which the chemical force strives, a maximum from which the deviations in most cases are small, although in others they may be very large; and I maintain that this view of the subject, which the memoir has aimed to establish, is supported by the analogies of nature.

---

* I have used the term *phenomenal laws* to designate a class of laws of nature which are empirical in their character, inasmuch as they are obviously not ultimate, although their derivation has not been discovered, but which are more universal than those to which the term *empirical* is commonly applied.

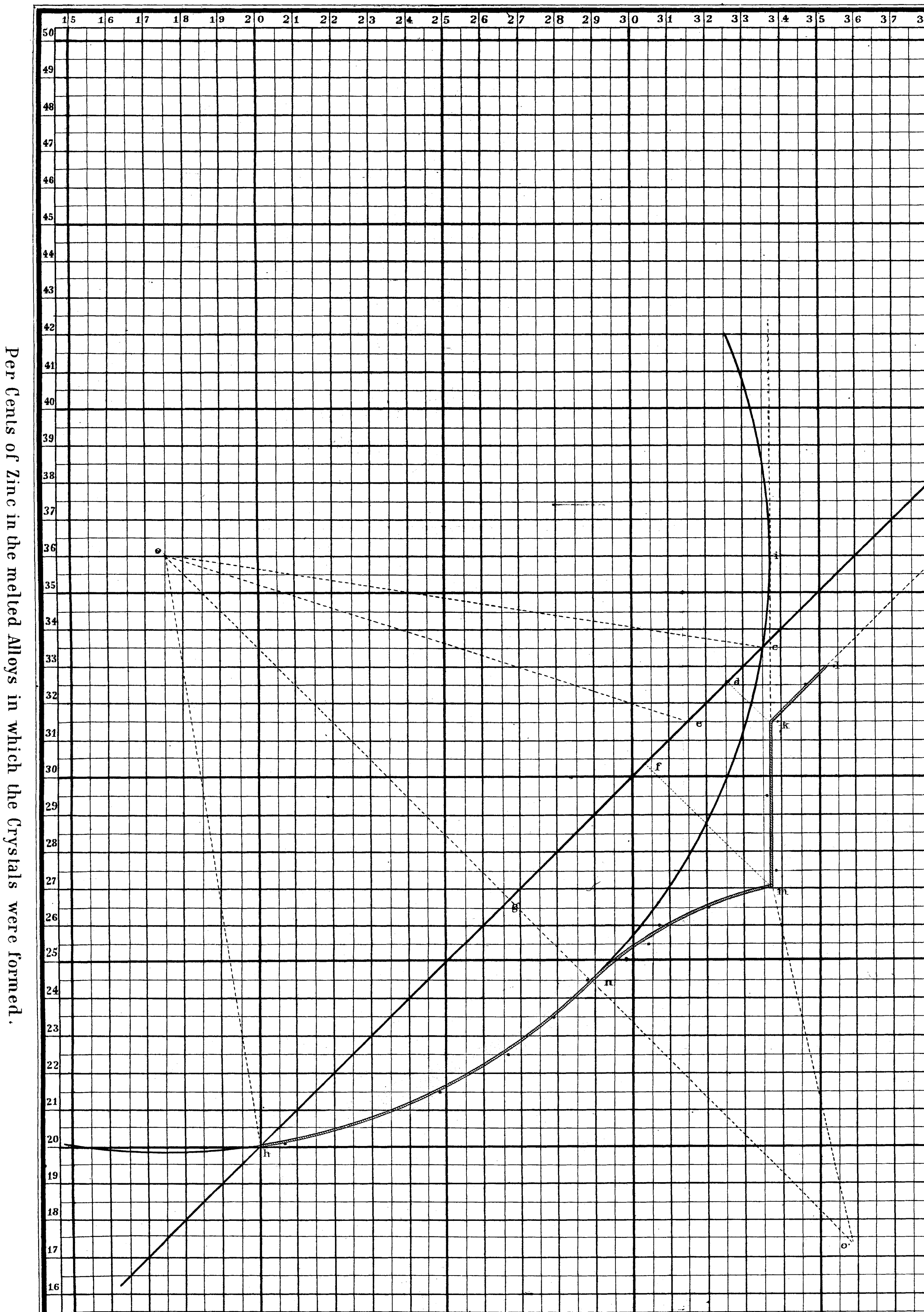
When the dynamical law has been discovered, of which the phenomenal law was merely the outward manifestation, as Kepler's laws were merely the phenomena of the law of universal gravitation, the very variations have been seen to be necessary consequences of the law itself; and if ever the dynamical law which governs chemical phenomena shall be discovered, it is most probable that the variations from the law of definite proportions will become as much a matter of calculation as the perturbations of astronomy. In both cases the perturbation is apparently due to the influence of an extraneous mass of matter.

The argument from analogy becomes stronger when we consider the equivalent numbers. I have shown in a former memoir,* that these numbers may be connected by a very simple numerical law; but here, as in other cases, we find merely a tendency towards the law, not an absolute agreement with it, the differences between the theoretical and the experimental equivalents being in many cases too great to be covered by errors of observation. The present memoir may throw light upon these discrepancies; for, to say the least, it is possible that the differences may originate in variations of the equivalent itself, and that the theoretical equivalent may be the maximum towards which the chemical force tends. On comparing carefully the different determinations of the chemical equivalents, many facts will be noticed supporting this view; those equivalents, for example, which coincide with, or very nearly approach, whole numbers, such as those of oxygen, carbon, and sulphur, will be found as a general rule to have been determined by the analysis or synthesis of compounds whose elements are united by a strong chemical force; also, when the equivalents have been determined by essentially

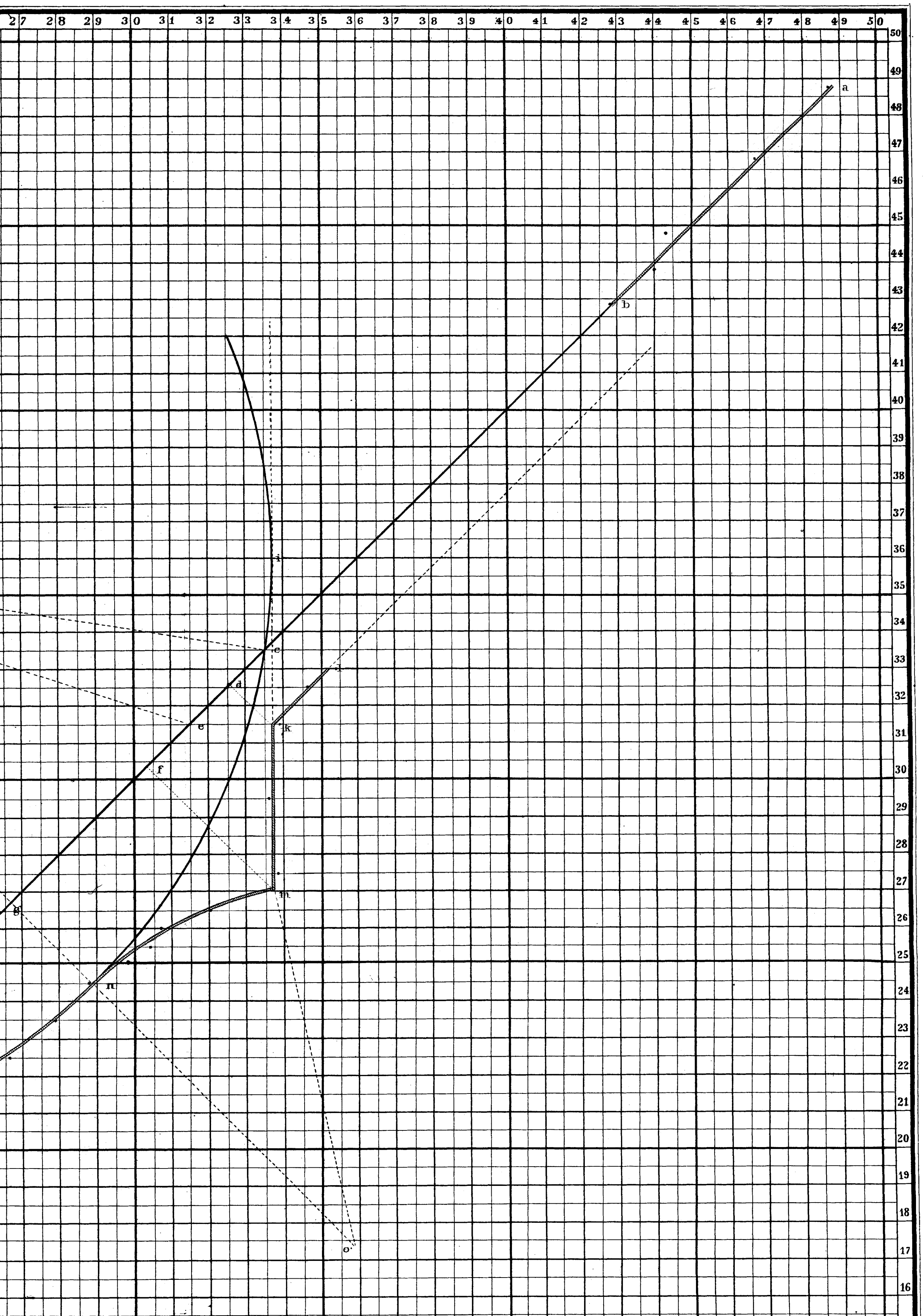
---

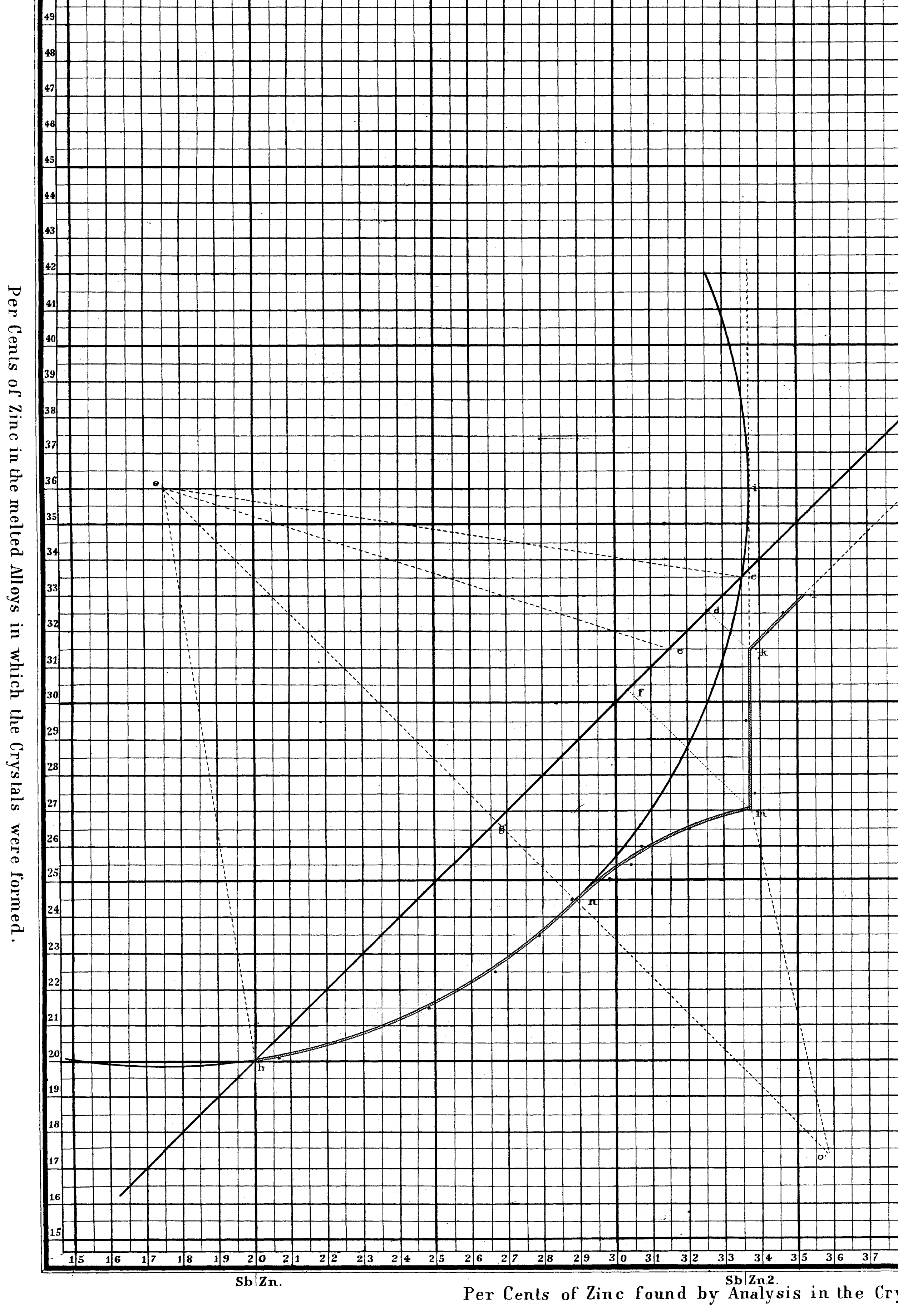
* This volume, page 235.

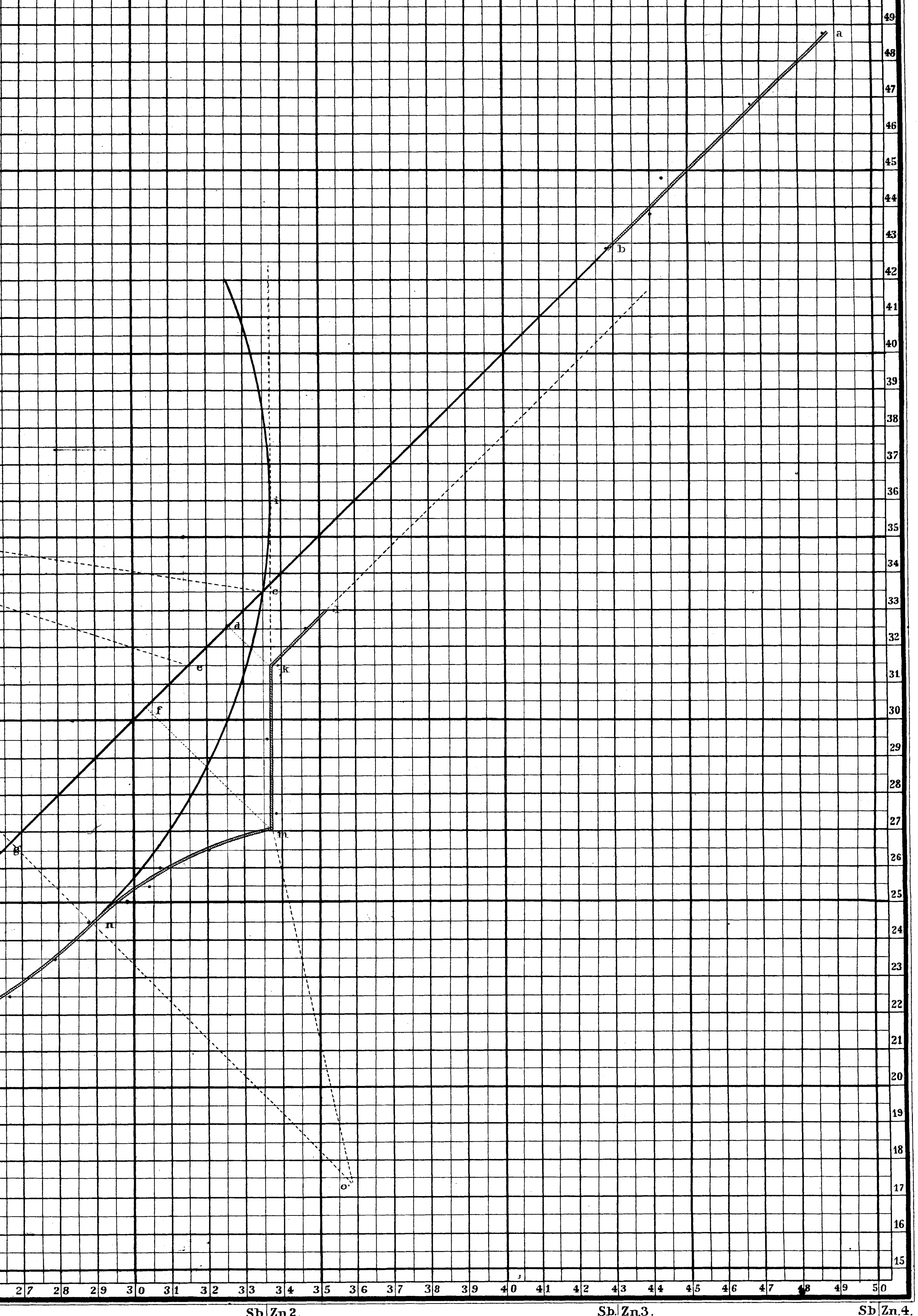
CURVE EXHIBITING THE VARIATION IN COMPOSITION OF THE CRYSTALS FORME



COMPOSITION OF THE CRYSTALS FORMED IN THE ALLOYS OF ZINC AND ANTIMONY.




Per Cents of Zinc in the melted Alloys in which the Crystals were formed.
49
48
47
46
45
44
43
42
41
40
39
38
37
36
35
34
33
32
31
30
29
28
27
26
25
24
23
22
21
20
19
18
17
16
15
a
i
c
d
e
k
f
g
m
n
h
o
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
Sb|Zn.
Sb|Zn2.
Per Cents of Zinc found by Analysis in the Cry



r Cents of Zinc found by Analysis in the Crystals.

different processes, it will be noticed that they seldom perfectly agree; so that, whatever view may be taken of the subject, it will now become a matter of the highest importance to ascertain how far, if at all, the determinations of the chemical equivalents have been influenced by similar causes to those which have produced the variations described in this memoir. This influence can only be detected by multiplying the determinations by as many different processes as possible, and submitting the results to a rigorous mathematical scrutiny.

If the doctrine of this memoir is correct, and the chemical equivalents are really liable to variation, it will have an important influence on chemical philosophy. The atomic theory, as at present interpreted by chemists, is irreconcilable with it, and our present ideas in regard to isomorphism must be materially changed. But it must be remembered, that the conclusions of the memoir are drawn from the examination of only two compounds, and therefore that it would be premature to dwell on these obvious consequences of the principle until it has been substantiated by further investigations. In conclusion, I would express my obligation to the gentlemen who have assisted me in the labor of the investigation, which, on account of the large number of analyses, has been very great, and could not have been concluded so soon had it not been for their very great industry and zeal.

Cambridge, July 20th, 1855.